Selenodemercuration of Phenyl- and p-Tolylmercury (II) Compounds

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Note

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It has previously been reported that arylthallium(III) compounds reacted with copper(II) selenocyanate to give aryl selenocyanate (selenocyanatodethallation).[1] We report here the results of the application of this reaction to phenyl- and *p*-tolylmercury(II) compounds which resulted in both selenocyanato- and selenodemercurations.

When phenylmercury(II) acetate was treated with copper(II) selenocyanate in dioxane at reflux for 0.5 h, phenyl selenocyanate (**1**) was formed only in a low yield, accompanied by a formation of diphenyl selenide (**2**). The yields of both products were increased by prolonging the reaction time, the formation of diphenyl diselenide (**3**) being also observed(Scheme 1).[2] It has been reported that ferrocenylmercury(II) chloride reacted with copper(II) selenocyanate in acetonitrile to give the corresponding

$$\mathrm{PhHgOAc} \xrightarrow[\text{Dioxane or MeCN}]{\mathrm{Cu(SeCN)_2}} \underset{(\mathbf{1})}{\mathrm{PhSeCN}} + \underset{(\mathbf{2})}{\mathrm{PhSePh}} + \underset{(\mathbf{3})}{\mathrm{PhSeSePh}} \qquad (1)$$

selenocyanate and diselenide in good yields.[3] When we carried out the above reaction in acetonitrile as solvent instead of dioxane, no significant improvements were observed except that the yield of products were slightly high.

Treatment of phenylmercury(II) acetate with a mixture of copper(II) sulfate and potassium selenocyanate gave mainly **2** and **3**, while phenylmercury(II) chloride reacted with the mixture to give almost equal amounts of **1**, **2**, and **3** under similar conditions. *p*-Tolylmercury(II) bromide also reacted with $CuSO_4$/KSeCN to afford a mixture of *p*-tolylselenocyanate, di-*p*-tolyl selenide, and di-*p*-tolyl diselenide. Typical results are shown in Table I. As compared to the reactions of arylthallium(III) compounds with $Cu(SeCN)_2$ or $CuSO_4 \cdot 5H_2O$/KSeCN,[1] the reactions of arylmercury(II) compounds were revealed to be not so fruitful for the preparation of either **1**, **2**, or **3** because of a low yield and a low selectivity. Similar phenomenon

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Table I. Reaction of Arylmercury(II) Compounds with $Cu(SeCN)_2$ or $CuSO_4 \cdot 5H_2O$/KSeCN[a]

ArHgX (5 mmol)	$Cu(SeCN)_2$ (mmol)	$CuSO_4 \cdot 5H_2O$ (mmol)	KSeCN (mmol)	Solvent (25 ml)	Time (h)	Product and Yield (mmol) 1	2	3
PhHgOAc	10	0	0	Dioxane	0.5	0.30	0.12	0
PhHgOAc	10	0	0	Dioxane	5	1.04	0.20	0
PhHgOAc	10	0	0	Dioxane	24	1.60	0.67	0.24
PhHgOAc	1.25	0	0	Dioxane	24	0.98	0.45	0
PhHgOAc	10	0	0	MeCN	24	1.99	1.10	0.07
PhHgOAc	0	10	40	Dioxane	2	0.19	0.83	1.21
PhHgOAc	0	2.5	10	Dioxane	2	0.10	0.36	0
PhHgOAc	0	10	40	Dioxane	5	0.40	0.62	0.87
PhHgCl	0	10	40	Dioxane	2	0.83	0.78	0.97
PhHgCl	0	10	40	Dioxane	5	1.35	0.80	0.90
p-TolylHgBr	0	10	40	Dioxane	2	1.11[b]	0.82[c]	0.16[d]

a) At reflux temperature.
b) p-$CH_3C_6H_4SeCN$.
c) $(p\text{-}CH_3C_6H_4)_2Se$.
d) $(p\text{-}CH_3C_6H_4Se)_2$.

has also been observed in the treatment of arylthallium(III) and arylmercury(II) compounds with copper(II) cyanide. Namely, arylthallium(III) compounds gave aryl cyanides in excellent yields, while the mercury one afforded those in very poor yields.[4]

It has been noted that ferrocenylmercury(II) chloride reacted with ferrocenyl selenocyanate to give diferrocenyl selenide almost quantitatively.[3] Therefore, one of the reasons why the yield of **1** was low and appreciable amounts of **2** and **3** were obtained seems to be the reaction of the initially formed **1** with the starting phenylmercury(II) compound under the reaction conditions. In order to clarify this point various reactions of **1** were examined. As a result it was revealed that **1** surely reacted with phenylmercury(II) acetate to give **2** and **3** in the presence or absence of copper(II) sulfate (Cu^{2+} apparently catalyzes the reaction) in dioxane at reflux temperature (Scheme 2), while **1** itself was rather stable and did not give any **2** and **3** in the absence of phenylmercury(II) acetate. On the other hand, it was clarified that phenylthallium-

$$\text{PhHgX} + \mathbf{1} \xrightarrow[\text{Dioxane}]{(CuSO_4 \cdot 5H_2O)} \mathbf{2} + \mathbf{3} \qquad (2)$$

(III) compound gave only a small amount of **2** and none of **3** under the conditions where the mercury(II) analogue afforded lots of **2** and **3**. Typical results are shown in Table II. The recovered yield of **1** and also the yield of **2** and **3** were not high in several cases. One reason seems to be the formation of some complexes between these compounds and metal salts as has already been clarified in the formation of coordination compounds with several transition metals.[5] Another reason may be due to the formation of phenylselenenic acid (PhSeOH) and more preferably phenylseleninic

Table II. Reaction of **1** with Phenylmercury(II)- or Phenylthallium(III) Compound, Copper(II) Sulfate or Mercury(II) Acetate[a)]

PhSeCN (**1**) (mmol)	$PhMX_n$ (mmol)	Metal Salt (mmol)	Time (h)	Product and Yield(mmol) Recovered **1**	**2**	**3**
5	PhHgOAc 5	$CuSO_4 \cdot 5H_2O$ 2	2	2.18	0.22	0.30
5	PhHgOAc 5	$CuSO_4 \cdot 5H_2O$ 5	5	1.25	0.18	1.48
5	PhHgOAc 5	—	5	3.78	0.04	0.69
5	PhHgCl 5	$CuSO_4 \cdot 5H_2O$ 5	5	4.73	0.02	0.25
5	PhTl(OAc) $ClO_4 \cdot H_2O$ 5	$CuSO_4 \cdot 5H_2O$ 10	5	1.15	0.04	0
5	—	$CuSO_4 \cdot 5H_2O$ 10	2	3.61	0	0
5	—	$Hg(OAc)_2$ 5	5	0.87	0	0.26
5	—	$Hg(OAc)_2$ 0.5	20	4.20	0	0.05

a) In dioxane (25 ml) at reflux temperature.

acid (PhSeOOH) which might be lost in aqueous layer. The oxidation of **1** to the latter acid with several oxidizing agents has been known.[6)]

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(2) All reactions and the treatment after the reaction were carried out as has been described in Ref. 1. GLC (Shimadzu 4BMPF; N_2 as carrier gas) analyses of the products were carried out by raising the column temperature from 120°C to 200°C [120°C→150°C (5°C/min) and then 150°C→200°C (10°C/min) on Apiezon Grease L (10%)-Neopak 1A (1 m) column with dibenzyl as internal standard.

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